Solid State Communications, Vol. 71, No. 1, pp. 65–69, 1989.
Printed in Great Britain.

0038-1098/89 $3.00 + .00
Maxwell Pergamon Macmillan plc

THE INFLUENCE OF THE (2 × 1) RECONSTRUCTION OF THE Si(1 0 0) SURFACE ON THE Si-$L_{2,3}$VV AUGER LINESHAPE

A.G.B.M. Sasse*, M.A. van her Hoef, H. Wormeester and A. van Silfhout

University of Twente, Faculty of Applied Physics, P.O. Box 217, 7500 AE, Enschede, The Netherlands

(*Received* 8 *March* 1989 *by S. Amelinck*)

The extreme surface sensitiveness of the Si-$L_{2,3}$VV Auger process and its ability to probe the atomic electron distribution in the direct neighbourhood of the $L_{2,3}$-core-hold makes this electron spectroscopic technique a candidate for investigations of the local changes in the electron distribution due to surface reconstruction. In this paper we show, explicitly, the influence of the (2 × 1) reconstruction of the Si(1 0 0) surface on the Si-$L_{2,3}$VV Auger lineshape. Furthermore, the calculated Auger lineshape will be compared with an experimentally obtained line profile.

1. INTRODUCTION

AUGER electron spectroscopy (AES) is a widely used technique for surface chemical element analysis [1]. Earlier studies [2–12] showed that analysis of the lineshape of the Core Valence Valence (CVV) Auger spectrum can provide information of the local chemical environment of the target atomic species. However, the CVV Auger intensity, A(E), becomes distorted by all kind of losses such as elastic and inelastic scattering, interaction with collective oscillations (plasmons, etc.) and instrumental broadening [13–16]. It is well established that corrections of these Auger lineprofiles distortions are of sufficient quality to compare these results with the theory [16–22] as developed by Feibelman *et al.* [3] and Jennison [19, 20].

The aim of this paper is to show explicitly the significance of the influence of the 2 × 1 reconstruction of the Si(1 0 0) surface on the Si-$L_{2,3}$VV Auger lineshape.

Within the independent particle approximation, Feibelman *et al.* [3], showed that the Auger lineshape can be expressed in terms of atomic Auger matrix elements and of the atomic angular momentum components of the local density of states (LDOS) localized on the same site as the core-hole. In general the Auger lineshape will reflect the local electron distribution of an excited system, but in the case of silicon the Auger lineshape will probe approximately the ground state LDOS [2, 19–23]. Therefore, we can express the auger lineshape in terms of convolution products of the partial LDOS (pLDOS):

$$A(E) = C_{ss}N_s(E) * N_s(E) + C_{sp}N_s(E) * N_p(E) + C_{pp}N_p(E) * N_p(E) \quad (1)$$

$C_{kn}(n, k = s, p)$ are the two electron atomic Auger matrix elements and $N_k(E)$ are the k-like partial LDOS at the atom in which the initial hole is created.

It has been shown that for covalent molecules, for example Si, the interatomic Auger matrix elements can be neglected [20, 23]. This extreme local behaviour of the Auger process enables us to model half-infinite Si(1 0 0)2 × 1 reconstructed surface in terms of a finite cluster of silicon atoms. Moreover, we can perform quantum chemical cluster calculations to obtain the partial LDOS of a surface silicon atom and calculate its CVV Auger lineshape A(E) [21, 22, 24, 25], applying equation (1). One of the main advantages of this type of calculations is the possibility to evaluate

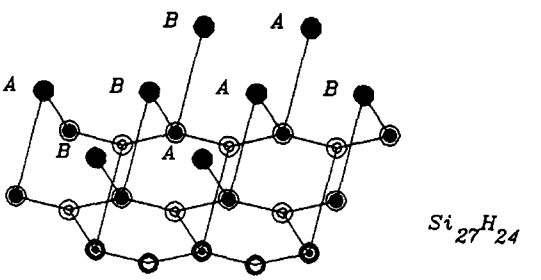

Fig. 1. The $Si_{27}H_{24}$ cluster; all unsaturated silicon bonds below the top layer are saturated with hydrogen atoms. The unsaturated bonds in the top layer, forming the dangling bonds, are subject to surface reconstruction; A is the down atom; B is the up atom of the dimer. The values of [29, 30] have been sued for the 2 × 1 reconstruction.

* Present address: Foundation for Advanced Metals Science, P.O. Box 8039, 7550 KA Hengelo (oV), The Netherlands.

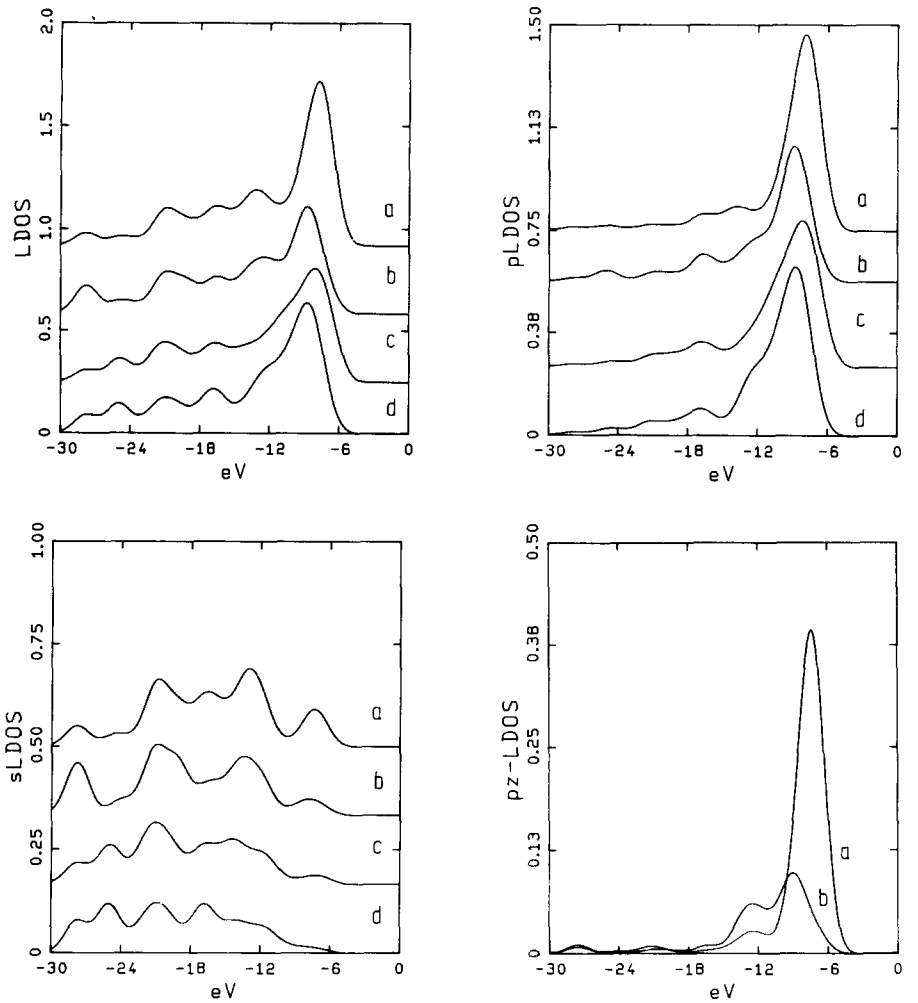

Fig. 2. Shown is the calculated LDOS and the *s*, *p*LDOS of the $Si_{27}H_{24}$ cluster. The densities are calculated from the Si-atoms at the top. In all figures we denote: (a) up-atom; (b) down-atom; (c) backbond connected to the up-atom; (d) backbond connected to the down-atom. LDOS (left top); *p*LDOS (right top); *s*LDOS (left bottom); P_z-LDOS (right bottom). The vacuum level is the zero of the energy scale.

the influence of surface geometry in our Auger lineshape [24–29]. We can model the 2 × 1 reconstruction of the surface in terms of its related surface bonds, such as the filled and empty dangling bond, the dimerbond and the backbond.

The Si–$L_{2,3}$VV Auger spectra were recorded under the following operation conditions: The primary electrons were accelerated to 2000 eV with a Wallis PM4DCP (10–4000) high voltage unit; primary current density of 100 $\mu A\,cm^{-2}$; modulation of the RFA detector is $2\,V_{p-p}$; sweep rate between 0.05–0.5 $eV\,s^{-1}$. The Auger spectra were recorded between 15–115 eV in the first derivative mode (dN(E)/dE) of the kinetic energy distribution of the Auger electrons by using a PAR lock-in amplifier with a lock-in time constant $\leqslant 1$ s. The $dN(E)/dE$ Auger spectra were stored digital.

The surface cleaning is performed by repeated argon-sputtering (800 eV) and annealing at 600° C during sputtering and annealing of 1 h at 800° C after the sputter cycles [30]. The surface was considered to be clean when no elements other than Si could be detected in the Auger KLL spectrum.

The scheme for correction of the distortion of the lineprofile of the measured kinetic energy distribution, $N(E)$, is discussed extensively elsewhere [15]. Using this method we can calculate the dA(E)/dE from the measured dN(E)/dE.

The Si(1 0 0)2 × 1 reconstructed surface, is modeled by a $Si_{27}H_{31}$ cluster (see Fig. 1). For the subsurface atoms the ideal bulk geometry of silicon (i.e. d_{Si-Si} = 2.35 Å, and tetrahedral angles) has been used, whereas the surface atoms are subject to an asymmetric 2 × 1 reconstruction [28, 29] as reported

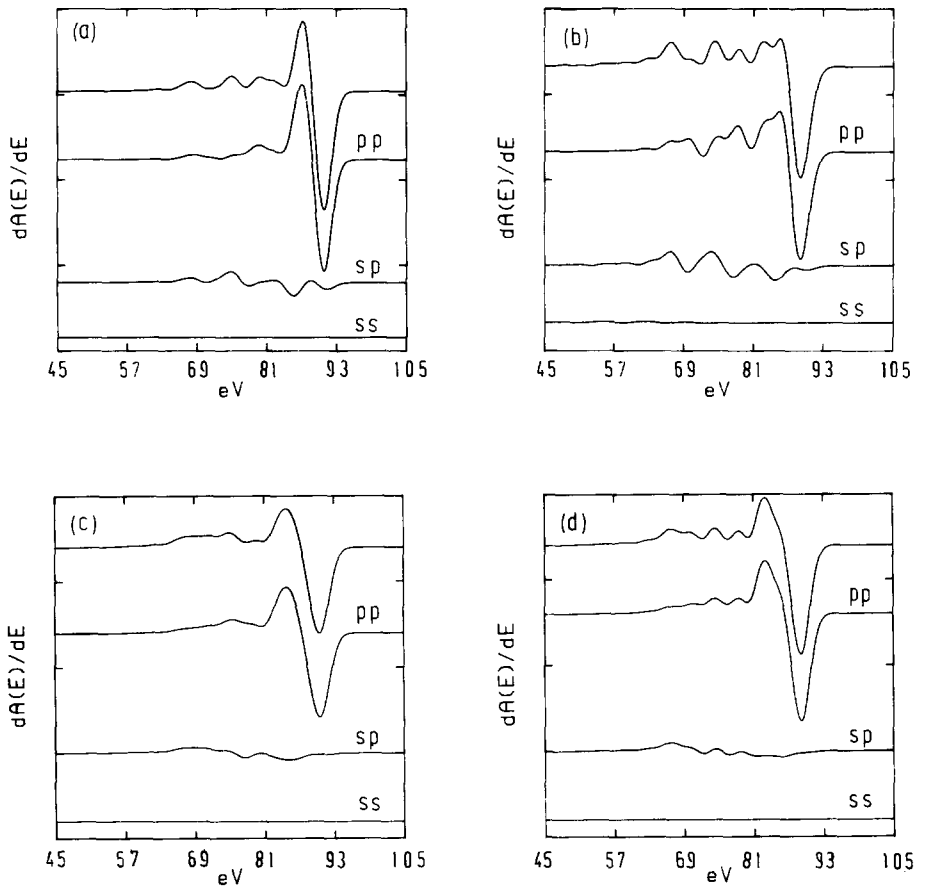

Fig. 3. Shown is here the influence of different types of surface atoms on the Auger spectra. (a) dimer-up; (b) dimer-down backbond; (c) connected to dimer-up and (d) backbond connected to dimer-down.

by Kunjunny and Ferry [31]. We used hydrogen atoms to terminate the silicon substrate and obtaining boundary conditions of sufficient quality. We have adapted the Si–H bond length, $d_{\text{Si-H}} = 1.41$ Å, found by Estreicher [32].

The calculated discrete local density of states at atom X are broadened with Gaussians, resulting in a LDOS

$$\varrho_x(E) = (\pi\sigma^2)^{-1/2} \sum_A^x \left[\sum_\mu |c_{A\mu}|^2 \right] \exp\left(-(E - \varepsilon_A)/\sigma^2\right). \tag{2}$$

The summation μ and A runs over all atomic orbitals on atom X and over the one-electron wavefunctions (ϕ_A), respectively. ε_A is the energy of this one-electron wavefunction ($\phi_A = \Sigma_\mu c_{A\mu}\chi_\mu$). The most commonly used value for σ is 1 eV [26, 27]. The LDOS can be splitted into its atomic angular components (s, p), yielding the partial LDOS (pLDOS).

The results of the pLDOS calculations are depicted in Fig. 2. These results are discussed elsewhere [33] and are found in a good agreement with the results of others.

In our calculations we have approximated the two electron Auger matrix elements $C_{k,l}$ by the ratio of the possible decay channels (pp: 46, sp: 24, ss: 3) for the Auger electrons [19, 20]. Because, the atomic Auger matrix elements, do not vary much as function of energy [2, 3] and contribute only to the peak intensity in the $A(E)$ spectrum and not to the peak position. The the number of the decay channels is governed by the selection rules of the atomic angular momentum of the electrons involved in the Auger process [3, 10, 19].

In Fig. 3 we depict the calculated spectra for the individual surface atoms, e.g. up- and down-atom of the dimer in the first layer and their backbond atoms. We recognize immediately the influence of the chemical configuration of the target atom, determining the 2 × 1 reconstruction, in the Auger lineshape. The main peak in the spectra can unambiguously be interpreted as a pp-Auger process and the sp-contributions are responsible for the structure in the low energy tail. The ss-contributions are neglectable in all spectra

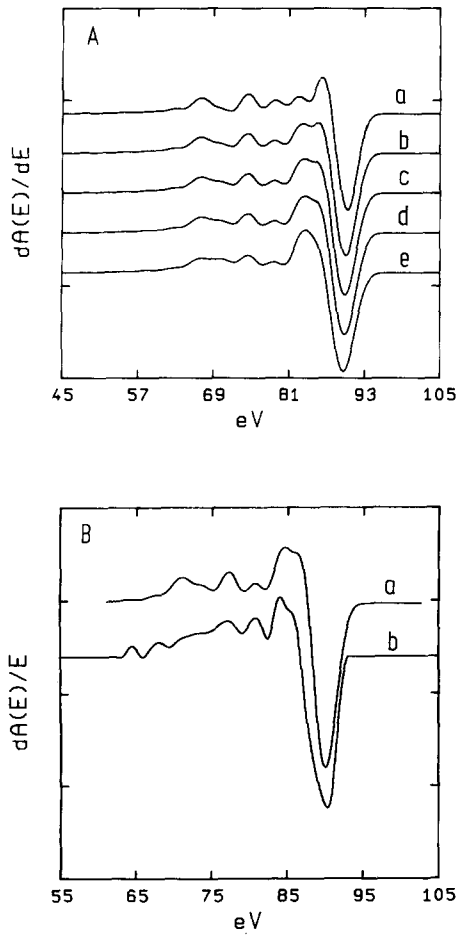

Fig. 4. (A) Calculated dA/dE spectrum as function of the ratio between dimer atoms and backbond atoms. The first number of the ratio is the number of dimer atoms and the second number the amount of backbond atoms involved in the calculation. (a) 1 : 0; (b) 1 : 1; (c) 1 : 2, (d) 1 : 3; (e) 0 : 1. (B) the measured loss corrected $dA(E)/de$ of the clean Si(1 0 0)2 × 1 reconstructed surface compared with calculated $dA(E)dE$ spectrum (Fig. 4(A)c).

depicted. Furthermore, we can reveal from our calculations, the difference between which atom is connected to the up atom in the dimer and which one to the down atom by inspecting the peak. This can be explained by an additional structure in the *p*LDOS at −8 eV below valence band maximum at the down atoms, which can be attributed to electrons involved in the dimer bond, which is characteristic for the 2 × 1 reconstruction.

Before we can compare the calculated and measuredAuger lineshape A(E) in the derivative mode we need to sum the individual atomic Auger lineshapes shown in Fig. 3 with respect to the probing depth. In our experimental setup this probing depth is about a few atom layers. We notice in Fig. 4, that the difference in the structure of the individual atomic contribution (e.g. backbond atoms and dimer atoms) are blurred in the weighted Auger lineshape. Although, slight differences can be seen in the calculated weighted Auger lineshapes, Fig. 4, we believe that these differences are not prominent enough in the experimentally obtained curve (Fig. 4b) to identify unambiguously the differences into the local atomic electron distribution. Therefore, Auger electron spectroscopy cannot be used successfully as a spectroscopic technique for investigating differences in the silicon surface bonding due to the (2 × 1) reconstruction of the Si(1 0 0) surface and is also questionable for other silicon surfaces.

Nevertheless we observe a good agreement between the calculated and experimentally obtained Auger lineshape. More fine structure can be resolved additional to the well established Auger transitions at 91.8 and 81 eV [12]. The low energy tail of the experimentally obtained spectrum is slightly overestimated due to the data processing, which is worse in this energy region.

In summary, we showed that their exist an influence of the 2 × 1 reconstruction of the Si(1 0 0) surface for the individual silicon atoms in the surface region. But these differences become blurred by its summation with respect to the probing depth. Therefore, these difference cannot be used to analyze surface bonding unambiguously.

REFERENCES

1. P.H. Holloway, *Adv. Electron. Electron Phys* **54,** 241 (1980).
2. D.E. Ramaker, *Springer Series in Chemical Physics*, Vol. 20 (Edited by R. Vanselow and R. Howe), Springer, Berlin, (1982) p. 19; D.E. Ramaker, F.L. Hutson, N.H. Turner & W.N. Mei, *Phys. Rev.* **B33,** 2574 (1986).
3. P.J. Feibelman, E.J. McGuire & K.C. Pandey, *Phys. Rev.* **B5,** (1977) 2202; P.J. Feibelman & E.J. McGuire, *Phys. Rev.* **B17,** 690 (1978).
4. D.E. Ramaker, J.S. Murday, N.H. Turner, C. Moore, M.G. Lagally & J.E. Houston, *Phys. Rev.* **B19,** 5375 (1979).
5. J.J. Lander, *Phys. Rev.* **91,** 1382 (1953).
6. H.D. Hagstrum & G.E. Becker, *Phys. Rev.* **B4,** 4187 (1971).
7. H.D. Hagstrum & G.E. Becker, *Phys. Rev.* **B8,** 1580 (1973).
8. G.F. Amelio, *Surface Sci.* **22,** 301 (1970).
9. J.E. Houston, *J. Vac. Sci. Technol.* **12,** 255 (1974).
10. R. Weissmann & K. Muller, *Surf. Sci. Retp.* **1,** 251 (1981).
11. R.H. Brockman & G.J. Russel, *Phys. Rev.* **B22,** 6302 (1980).

12. A.G.B.M. Sasse, D.G. Lakerveld & A. van Silfhout, *J. Vac. Sci. & Technol.* **195,** L167 (1988).
13. D.E. Ramaker, *Appl. Surf. Sci.* **21,** 243 (1985).
14. W.M. Mularie & W.T. Peria, *Surf. Sci.* **26,** 125 (1971).
15. A.G.B.M. Sasse, H. Wormeester & A. van Silfhout, *Surface and Interf. Anal.* **13,** 228 (1988); H. Wormeester, A.G.B.M. Sasse & A. van Silfhout, *Commuter Phys. Comm.* **52,** 19 (1988); A.G.B.M. Sasse, H. Wormeester & A. van Silfhout, *J. Vac. Sci. & Technol. A* (in press).
16. H.H. Madden & J.E. Houston *J. Vac. Sci. & Technol.* **47,** 3071 (1976).
17. H.H. Madden & J.E. Houston, *Solid State Commun.* **21,** 1081 (1977).
18. H.H. Madden & J.E. Houston, *J. Vac. Sci. Technol.* **14,** 412 (1977).
19. D.R. Jennison, *Phys. Rev.* **B18,** 6865 (1978).
20. D.R. Jennison, *Phys. Rev. Lett.* **40,** 807 (1987).
21. D.E. Ramaker, *Phys. Rev.* **B25,** 7341 (1982).
22. D.E. Ramaker, *Phys. Rev.* **B21,** 4608 (1980).
23. J.A.D. Matthew & Y. Komninos *Surf. Sci.* **53,** 716 (1975).
24. M.J.S. Dewar, R.C. Bingham & D.H. Lo, *J. Amer. Chem. Soc.* **97,** 1285 (1975).
25. P. Bischof, *J. Amer. Chem. Soc.* **98,** 6844 (1976); J. Ihm, *Rep. Prog. Phys.* **51,** 105 (1988).
26. R.P. Messmer, *The Nature of Surface Chemical Bond* (Edited by Rhodin and Ertl), North Holland Publ. Amsterdam (1979).
27. G. De Meyer, R. Hoogewijs, W. Lambrecht & J. Vennik, *Solid State Commun.* **33,** 267 (1980).
28. D.J. Chadi, *Phys Rev. Let.* **43,** 43 (1979).
29. W.S. Verwoerd, *Surf. Sci.* **99,** 581 (1980).
30. E.G. Keim, L. Wolterbeek & A. van Silfhout, *Surf. Sci.* **180,** 565 (1987).
31. T. Kunjunny & D.K. Ferry, *Phys. Rev.* **B24,** 4593 (1981).
32. S. Estreicher, *Phys. Rev.* **B37,** 858 (1988).
33. A.G.B.M. Sasse & A. van Silfhout, *Phys. Rev.* **B** (in press); A.G.B.M. Sasse, H. Wormeester, M.A. van der Hoef, A. van Silfhout & E.G. Keim, *J. Vac. Sci. Technol. A* (in press).